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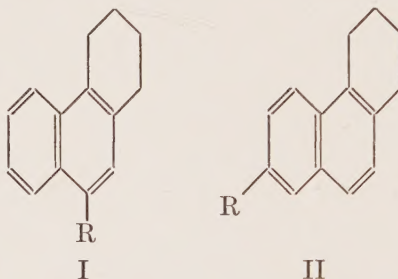
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REACTIONS OF TETRAHYDROPHENANTHRENE. II

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In continuation of work on the reactions of 1,2,3,4-tetrahydrophenanthrene (1), the hydrocarbon has been subjected to bromination, chloromethylation, benzoylation (Perrier reaction), and a modified Friedel-Crafts reaction with acetyl chloride and with propionyl chloride. From the products so obtained various derivatives of tetrahydrophenanthrene have been prepared. In all cases, substitution was predominantly in the 9 position.



By means of the Friedel-Crafts reaction between 1,2,3,4-tetrahydrophenanthrene and acetyl chloride in nitrobenzene, in addition to the 9-acetyltetrahydrophenanthrene (I, R = COCH₃) which had been obtained previously, the 7 isomer (II, R = COCH₃) was isolated; the ratio of the 9 to the 7 isomer was about 2:1. The structure of the isomer was proved by reduction to 7-ethyl-1,2,3,4-tetrahydrophenanthrene (II, R = CH₂CH₃) followed by dehydrogenation to 2-ethylphenanthrene. Further proof for the location of the acetyl group in the 7 position in this isomer was obtained by conversion to the previously identified β -7-(1,2,3,4-tetrahydrophenanthroyl)propionic acid (II, R = COCH₂CH₂COOH) (2). When a mixture of tetrachloroethane and carbon bisulfide was used as solvent for the acetylation in such a proportion that an aluminum chloride addition complex of the product precipitated, the 9-acetyl derivative was obtained free from the 7 isomer.

Propionyl chloride was employed in this same manner to yield 9-propionyl-1,2,3,4-tetrahydrophenanthrene (I, R = COCH₂CH₃). This was reduced by the Clemmensen method to 9-propyl-1,2,3,4-tetrahydrophenanthrene (I, R = CH₂CH₂CH₃) which was converted to the known 9-propylphenanthrene by dehydrogenation.

The product obtained by benzoylation of 1,2,3,4-tetrahydrophenanthrene by the Perrier modification of the Friedel and Crafts reaction proved to be 9-benzoyl-1,2,3,4-tetrahydrophenanthrene. Beckmann rearrangement of its oxime gave the anilide of 1,2,3,4-tetrahydrophenanthrene-9-carboxylic acid

¹ From the Ph.D. dissertation of M. W. Cronyn.

(I, R = CONHC₆H₅) which was identical with the anilide of the acid obtained by hypochlorite oxidation of 9-acetyl-1,2,3,4-tetrahydrophenanthrene.

Bromination of 1,2,3,4-tetrahydrophenanthrene yielded 9-bromo-1,2,3,4-tetrahydrophenanthrene, (I, R = Br), which was converted to 9-cyano-1,2,3,4-tetrahydrophenanthrene (I, R = CN) in 80% yield by reaction with cuprous cyanide. Hydrolysis of the resulting nitrile gave the 9-carboxylic acid (I, R = COOH).

Chloromethylation of 1,2,3,4-tetrahydrophenanthrene by the procedure employed by Grummitt and Buck (3) on naphthalene gave a crystalline monochloromethyl derivative, which was identified as 9-chloromethyl-1,2,3,4-tetrahydrophenanthrene (I, R = CH₂Cl) by its reaction with malonic ester to give the 9-propionic acid (I, R = CH₂CH₂COOH). This acid was identical with the propionic acid obtained by sodium amalgam reduction of the acrylic acid (I, R = CH=CHCOOH) produced from the reaction between malonic acid and the aldehyde (I, R = CHO) derived from the 9-acid anilide by the Sonn-Müller method. In addition, reaction of the 9-chloromethyl derivative with sodium cyanide and hydrolysis of the resulting nitrile gave 1,2,3,4-tetrahydrophenanthrene-9-acetic acid (I, R = CH₂COOH) identical with the acid obtained by means of the Willgerodt reaction from 9-acetyl-1,2,3,4-tetrahydrophenanthrene.

Beckmann rearrangement of the oxime of 9-acetyl-1,2,3,4-tetrahydrophenanthrene gave 9-acetylamino-1,2,3,4-tetrahydrophenanthrene which was hydrolyzed to 9-amino-1,2,3,4-tetrahydrophenanthrene (I, R = NH₂). A small amount of the 7-amino-1,2,3,4-tetrahydrophenanthrene (II, R = NH₂) was prepared in a similar manner by hydrolysis of the corresponding acetylamine which was separated from the mixture of acetylaminos obtained by rearrangement of a mixture of the oximes of the 7- and 9-acetyl derivatives.

1,2,3,4-Tetrahydrophenanthrene-7-acetic acid (II, R = CH₂COOH) was obtained by the Willgerodt reaction from the 7-acetyl derivative. 1,2,3,4-Tetrahydrophenanthrene-7-carboxylic acid (II, R = COOH) was separated from a mixture of the 7- and 9-acids resulting from hypochlorite oxidation of a mixture of 7- and 9-acetyl derivatives.

By cyclizing the acid chloride of 1,2,3,4-tetrahydrophenanthrene-9-acetic acid with aluminum chloride, 4-keto-7,8,9,10-tetrahydroacephenanthrene (III) was obtained. Clemmensen reduction converted the ketone to 7,8,9,10-tetrahydroacephenanthrene (IV). Fieser and Peters (4) prepared this hydrocarbon from acenaphthene.



EXPERIMENTAL

Preparation of 1,2,3,4-tetrahydrophenanthrene. A mixture of γ -(1- and 2-naphthyl)-butyric acids (208 g.), prepared as described (1) and 222 g. of phosphorus pentachloride in 900 cc. of dry benzene was allowed to stand at room temperature for one hour and then warmed for five minutes on a steam-cone. To the solution, cooled to 5° in an ice-salt bath, a cold solution of 240 cc. of stannic chloride in 240 cc. of benzene was added with stirring at such a rate that the temperature did not rise above 10° (twenty-five minutes). After an additional thirty-five minutes of stirring, the mixture was hydrolyzed by stirring it cautiously into crushed ice and dilute hydrochloric acid. Vacuum distillation of the product gave 162 g. (85%) of a mixture of 1- and 4-ketotetrahydrophenanthrene. Reduction of 225 g. of the mixture of the cyclic ketones by the method described (1) gave 188 g. (90%) of 1,2,3,4-tetrahydrophenanthrene (b.p. 118–120° at 0.1 mm.), which crystallized on cooling.

9-Acetyl-1,2,3,4-tetrahydrophenanthrene. To a suspension of 16.5 g. of anhydrous aluminum chloride in 200 cc. of carbon bisulfide was added 10 g. of acetyl chloride and the mixture was then stirred for fifteen minutes. After the addition of 130 cc. of *sym*-tetrachloroethane, the solution was stirred for another fifteen minutes, then warmed for about five minutes up to 45–50° until all the aluminum chloride had dissolved to give a clear, greenish-yellow solution. The solution was cooled to 15°, and 11 g. of 1,2,3,4-tetrahydrophenanthrene dissolved in 20 cc. of carbon bisulfide was added. Before addition of the hydrocarbon had been completed, hydrogen chloride was evolved, the solution became dark, and within a few seconds it was filled with a thick gelatinous precipitate of the aluminum chloride-ketone addition complex. Stirring was continued for half an hour at room temperature and then the mixture was placed in a refrigerator for twenty-four hours. The cold mixture was filtered and the canary-yellow crystalline complex (23–24 g.) was washed with carbon bisulfide, and then spread out on filter paper for a few minutes to allow the carbon bisulfide to evaporate. The solid was added in portions with stirring to 5% hydrochloric acid solution and crushed ice, and the cream colored lumps of ketone were broken up, filtered, washed thoroughly with water, and dried; yield 11.8–12.2 g. (87–90%); m.p. 52–55°. This was sufficiently pure for most reactions. A purer product was obtained by distilling the ketone under reduced pressure (b.p. 163–166° at 0.1 mm.) and recrystallizing from ethanol; yield 10.6–11.0 g. of colorless prisms; m.p. 56.5–58°. An additional 0.5–0.7 g. of pure ketone was recovered from the carbon bisulfide solution, bringing the total yield to 83–86%.

7-Acetyl-1,2,3,4-tetrahydrophenanthrene. After dissolving 30 g. of anhydrous aluminum chloride in 150 cc. of nitrobenzene cooled to 5°, 12 g. of acetyl chloride was added, the solution was cooled further to –15°, and a solution of 20 g. of 1,2,3,4-tetrahydrophenanthrene in 25 cc. of nitrobenzene was added dropwise with good stirring. The stirring was continued for half an hour at –15°, and for two hours up to 0°, and the mixture then placed in a refrigerator for forty-eight hours. Vacuum distillation of the residue after hydrolysis and steam distillation of the nitrobenzene yielded 21.3 g. of a mixture of the 7- and 9-acetyl derivatives and some tetrahydrophenanthrene. This oily product was dissolved in 175 cc. of absolute methanol, the solvent was removed with a current of air until the first drops of oil appeared, and the solution then seeded with 9-acetyl-1,2,3,4-tetrahydrophenanthrene and placed in a refrigerator for twenty-four hours. After removing the first crop of large prisms of the 9-acetyl derivative (7.2 g., m.p. 55–57°), a current of air was passed over the solution until crystals of the 7-acetyl derivative separated in the form of stubby needles. In one run these separated spontaneously in the filtrate from the first crop. After standing in the cold several days, a total of 4.7 g. was obtained, m.p. 85–89°. Further crystallization gave another 2 g. of the 9-acetyl derivative. Although more crystalline product could not be obtained, the residue was suitable for reactions in which the isomeric products could be separated, such as hypochlorite oxidation of the ketones and Beckmann rearrangement of the oximes. Two recrystallizations from ethanol of 7-acetyl-1,2,3,4-tetrahydrophenanthrene gave fine colorless needles, m.p. 90.5–91.5°.

Anal. Calc'd for $C_{16}H_{16}O$: C, 85.7; H, 7.2.

Found: C, 85.8; H, 7.3.

7-Ethyl-1,2,3,4-tetrahydrophenanthrene. A mixture of 1 g. of 7-acetyl-1,2,3,4-tetrahydrophenanthrene, 5 g. of amalgamated zinc, 10 cc. of acetic acid, 10 cc. of hydrochloric acid, and 4 cc. of toluene was refluxed for twenty-four hours with the addition of 6 cc. of hydrochloric acid during that time. The product after evaporative distillation at low pressure was a colorless oil; yield 0.9 g.

Anal. Calc'd for $C_{16}H_{18}$: C, 91.4; H, 8.6.

Found: C, 91.1; H, 8.7.

The *picrate* was obtained as light yellow needles from ethanol; m.p. 90–91°.

Anal. Calc'd for $C_{22}H_{21}N_3O_7$: N, 9.6. Found: N, 9.7.

A 0.27-g. sample of the above hydrocarbon was heated with 0.04 g. of palladium-charcoal catalyst (5) for one hour at 300–320°. After benzene extraction, filtration, and removal of the benzene, the residue was crystallized from ethanol; yield 0.23 g. (87%) of pearly leaflets; m.p. 64–65°. Two recrystallizations from ethanol raised the melting point of the 2-ethylphenanthrene to 65–66°. The *picrate* was obtained as yellow needles from ethanol; m.p. 93.5–94.5°. Previously reported values for the hydrocarbon and *picrate* respectively are 67–68° and 95.5–96° (6), and 64–65° and 92–93° (7).

ω-Bromo-7-acetyl-1,2,3,4-tetrahydrophenanthrene. To 1 g. of 7-acetyl-1,2,3,4-tetrahydrophenanthrene dissolved in 40 cc. of absolute ether cooled to –15° was added 0.74 g. of bromine in 20 cc. of ether. After one and one-half hours at –5° to –10°, a colorless crystalline product had separated. The ether was partially removed and the product collected; yield 0.95 g. (70%); m.p. 114.5–116°. After two recrystallizations from methanol a sample formed colorless needles; m.p. 115.5–116.5°.

Anal. Calc'd for $C_{16}H_{15}BrO$: Br, 26.4. Found: Br, 26.5.

β-7-(1,2,3,4-Tetrahydrophenanthroyl)propionic acid. After refluxing a mixture of 0.05 g. of sodium, 0.5 cc. of malonic ester, and 10 cc. of dry benzene for twenty-four hours, 0.39 g. of *ω*-bromo-7-acetyl-1,2,3,4-tetrahydrophenanthrene was added and the mixture was refluxed for twenty-four hours. The substituted malonic ester was hydrolyzed with 3 cc. of 40% potassium hydroxide solution, and the dicarboxylic acid was decarboxylated at 180° for half an hour. The warm melt was dissolved in benzene, the acid extracted with dilute potassium hydroxide, and the solution acidified after treatment with Norit. Two recrystallizations from acetone-petroleum ether gave clusters of colorless prisms; yield 0.22 g. (60%); m.p. 155.5–157°, alone and unchanged when mixed with an authentic sample (m.p. 158–159°) (2).

9-Benzoyl-1,2,3,4-tetrahydrophenanthrene. After warming 8 g. of benzoyl chloride and 7.5 g. of anhydrous aluminum chloride over a free flame for a few minutes, the melt was cooled somewhat and dissolved in 42 cc. of warm carbon bisulfide; then a solution of 10 g. of tetrahydrophenanthrene in 10 cc. of carbon bisulfide was added carefully in portions in order to avoid vigorous evolution of hydrogen chloride. After remaining in a refrigerator for twenty-four hours, a current of air was passed over the solution for a few minutes until the entire mass had solidified. The mixture was returned to a refrigerator for two hours, and then the brick-red complex was filtered, washed with cold carbon bisulfide, spread out to dry for a few minutes and then added to a 15% hydrochloric acid solution and cracked ice. The mixture was stirred until the complex was completely hydrolyzed and the colorless solid ketone was then filtered. Recrystallization from benzene-petroleum ether, after decolorization with Norit, gave 13.5 g. (86%) of thin colorless rectangular prisms; m.p. 119.5–121°. Two recrystallizations of a sample from ethanol gave prisms with the melting point 120–121°.

Anal. Calc'd for $C_{21}H_{18}O$: C, 88.1; H, 6.3.

Found: C, 87.9; H, 6.4.

9-Benzoyl-1,2,3,4-tetrahydrophenanthrene oxime. To a suspension of 20 g. of 9-benzoyl-1,2,3,4-tetrahydrophenanthrene in 300 cc. of absolute alcohol and 100 cc. of pyridine was added 20 g. of hydroxylamine hydrochloride and the mixture was refluxed for forty-eight hours; at no time did the solution become clear. After removing most of the solvent and pouring the residue into water, the oxime was filtered and crystallized from methanol; m.p. 225–227°; yield quantitative. Two recrystallizations of a sample from anhydrous ethyl acetate gave colorless prisms; m.p. 228–229°.

Anal. Calc'd for $C_{21}H_{19}NO$: N, 4.6. Found: N, 4.6.

1,2,3,4-Tetrahydrophenanthrene-9-carboxylic acid anilide. After refluxing 6.5 g. of the 9-benzoyl oxime and 5 g. of phosphorus pentachloride in 35 cc. of benzene for 15 minutes, the solution was poured into cold water with vigorous stirring until the anilide crystallized. After filtering the anilide from the benzene-water mixture, the benzene was washed with water, dried over anhydrous sodium sulfate, and evaporated to give further amounts of the anilide. The total yield amounted to 5.5 g. of fine needles; m.p. 238–241°, (85%). Two recrystallizations from anhydrous ethyl acetate gave colorless needles; m.p. 240–241°. The same compound resulted when the acid chloride of the 9-carboxylic acid (obtained by hypochlorite oxidation of the 9-acetyl derivative) prepared from the acid and phosphorus pentachloride was treated with aniline.

Anal. Calc'd for $C_{21}H_{19}NO$: N, 4.6. Found: N, 4.6.

9-Propionyl-1,2,3,4-tetrahydrophenanthrene. Only ten minutes stirring was required and no heating was necessary to effect solution of 8.5 g. of anhydrous aluminum chloride in 100 cc. of carbon bisulfide, 50 cc. of *sym*-tetrachloroethane and 5.7 g. of propionyl chloride. To this solution was added slowly with stirring a solution of 5.5 g. of 1,2,3,4-tetrahydrophenanthrene in 25 cc. of carbon bisulfide. An additional 25 cc. of carbon bisulfide was added and after a few minutes the addition complex started to separate. Stirring was continued for half an hour at room temperature and then the mixture was placed in a refrigerator for twenty-four hours. The canary yellow complex (9–10 g.) was worked up in the same manner as for the 9-acetyl derivative and gave 6 g. (83%) of ketone; m.p. 40–43°. Two recrystallizations from ethanol after distillation under reduced pressure (b.p. 160–162° at 0.05 mm.) gave colorless prisms; m.p. 43–44°.

Anal. Calc'd for $C_{17}H_{18}O$: C, 85.7; H, 7.6.

Found: C, 85.5; H, 7.8.

9-Propyl-1,2,3,4-tetrahydrophenanthrene. A mixture of 2 g. of 9-propionyl-1,2,3,4-tetrahydrophenanthrene, 10 cc. of toluene, 10 g. of amalgamated zinc, 15 cc. of hydrochloric acid, and 15 cc. of acetic acid was refluxed for twenty-four hours with the addition of 9 cc. of hydrochloric acid during this time. The product after evaporative distillation under reduced pressure crystallized from acetone-methanol in colorless needles; yield 1.75 g. (93%); m.p. 25–25.5°.

Anal. Calc'd for $C_{17}H_{20}$: C, 91.0; H, 9.0.

Found: C, 91.0; H, 9.0.

The *picrate* was obtained in orange needles from ethanol; m.p. 106–107°.

Anal. Calc'd for $C_{23}H_{23}N_3O_7$: N, 9.3. Found: N, 9.4.

A 0.25-g. sample of the above hydrocarbon was treated with 0.04 g. of palladium-charcoal catalyst for one hour at 300–320°. After benzene extraction, filtration, and removal of the benzene the 9-propylphenanthrene crystallized from ethanol in colorless needles; yield 0.20 g. (81%); m.p. 58.5–59.5°. Two recrystallizations failed to raise the melting point. The *picrate* was obtained from ethanol as yellow needles; m.p. 95.5–96°. Previously reported values for the hydrocarbon and *picrate* respectively are 57.5–58° and 98–99° (8), and 59° and 99° (9).

9-Bromo-1,2,3,4-tetrahydrophenanthrene. To a stirred ice-cooled solution of 5 g. of tetrahydrophenanthrene in 25 cc. of dry, thiophene-free benzene containing 0.5 g. of reduced iron powder as catalyst was added dropwise 5 g. of bromine in 10 cc. of dry benzene. The solution was kept cold for thirty minutes with stirring and then placed in a refrigerator for twelve hours, after which it was warmed for fifteen minutes on a steam-bath. The filtered solution was washed with dilute sodium carbonate and with water and dried. After removal of the solvent, the product was distilled under reduced pressure; b.p. 142–145° at 0.05 mm.; yield 6.4 g. (88%) of colorless liquid.

Anal. Calc'd for $C_{14}H_{13}Br$: Br, 30.6. Found: Br, 30.5.

The *picrate* was obtained from ethanol as light yellow needles; m.p. 102–103°.

Anal. Calc'd for $C_{20}H_{16}BrN_3O_7$: N, 8.6. Found: N, 8.7.

9-Cyano-1,2,3,4-tetrahydrophenanthrene. An intimate mixture of 3 g. of anhydrous cuprous cyanide, 2 cc. of pyridine, and 6.4 g. of 9-bromo-1,2,3,4-tetrahydrophenanthrene was heated at 215–225° for eighteen hours. The mixture was cooled somewhat, and poured

into 50 cc. of 15% ammonium hydroxide, and the dark lumps were mashed and stirred until a powder was obtained. The mixture was diluted and filtered, and the nitrile was evaporatively distilled at 190° and 0.1 mm. and then crystallized from acetone-petroleum ether from which it separated in colorless prisms; yield 4.1 g. (81%); m.p. 120–123°. After two recrystallizations from anhydrous ethyl acetate, it formed large prisms; m.p. 124–125°.

Anal. Calc'd for $C_{15}H_{13}N$: N, 6.8. Found: N, 6.8.

1,2,3,4-Tetrahydrophenanthrene-9-carboxylic acid. A mixture of 1 g. of 9-cyano-1,2,3,4-tetrahydrophenanthrene, 15 g. of potassium hydroxide, and 50 cc. of methanol was refluxed on a steam-cone for seven days. The alcohol was evaporated, the residue dissolved in water, and the solution filtered and acidified. In order to remove the silica, the acid was dried, dissolved in dilute bicarbonate solution, the solution filtered, and the acid reprecipitated; yield 1 g.; m.p. 206–210°. Sublimation and two recrystallizations from acetone gave colorless needles; m.p. 215–216°.

Anal. Calc'd for $C_{15}H_{14}O_2$: C, 79.6; H, 6.2.

Found: C, 79.4; H, 6.2.

The *methyl ester* obtained by means of diazomethane crystallized from methanol in colorless needles; m.p. 70.5–71°.

Anal. Calc'd for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7.

Found: C, 79.9; H, 6.7.

The acid and ester obtained by hypochlorite oxidation of the 9-acetyl derivative melted at 214–216° and 69–70° respectively, alone and when mixed with the acid and ester obtained from the nitrile.

9-Chloromethyl-1,2,3,4-tetrahydrophenanthrene. A mixture of 9 g. of tetrahydrophenanthrene, 2.8 g. of paraformaldehyde, 6.5 cc. of acetic acid, 9.1 cc. of hydrochloric acid, and 4.1 cc. of 85% phosphoric acid was stirred vigorously and heated for six hours at 80–85°. The product was poured into a separatory funnel, the lower acid layer was withdrawn and washed with ether, the ether was returned to the organic layer, more ether was added, and the ethereal solution was then washed twice with portions of cold water and dried with anhydrous potassium carbonate. After removal of the ether, the residue was distilled under reduced pressure; b.p. 163–165° at 0.05 mm.; yield 7 g. of colorless oil which crystallized after several hours. One recrystallization from acetone-ethanol gave thin flat needles; m.p. 60.5–61°. Two more recrystallizations failed to raise the melting point.

Anal. Calc'd for $C_{15}H_{15}Cl$: Cl, 15.4. Found: Cl, 15.5.

1,2,3,4-Tetrahydrophenanthrene-9-acetonitrile. To a solution of 2 g. of 9-chloromethyl-1,2,3,4-tetrahydrophenanthrene in 30 cc. of acetone was added a solution of 2 g. of potassium cyanide in 6 cc. of water and the mixture was refluxed for forty-eight hours. Ether and water were then added and the ether layer was separated, washed with water, and evaporated. The residue, after evaporative distillation under reduced pressure, crystallized from acetone in colorless prisms; yield 1.3 g.; m.p. 89–90°. After two more recrystallizations a sample melted at 89.5–90°.

Anal. Calc'd for $C_{16}H_{15}N$: N, 6.3. Found: N, 6.2.

1,2,3,4-Tetrahydrophenanthrene-9-acetic acid. (a) *From the nitrile.* A mixture of 1 g. of the 9-acetonitrile, 20 cc. of acetic acid, 9 cc. of hydrochloric acid, and 2 cc. of water was refluxed for twenty-four hours and then poured while hot into 30 cc. of hot concentrated hydrochloric acid. On cooling, the solution deposited 1 g. of colorless needles; m.p. 151–153°. Two recrystallizations from acetic acid raised the melting point to 153–153.5°.

Anal. Calc'd for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7.

Found: C, 80.3; H, 6.5.

(b) *From 9-acetyltetrahydrophenanthrene.* Using the Willgerodt method in the manner suggested by Fieser and Kilmer (10) except that the time of heating was twenty-four hours and the temperature 170°, 1.2 g. (56%) of 1,2,3,4-tetrahydrophenanthrene-9-acetic acid amide (m.p. 211–212°) was obtained from 2 g. of 9-acetyltetrahydrophenanthrene. After two recrystallizations from xylene the amide was obtained in colorless needles; m.p. 211.5–212.5°.

Anal. Calc'd for $C_{16}H_{17}NO$: N, 5.9. Found: N, 6.0.

The amide was hydrolyzed in the same manner as the corresponding nitrile. From 1.2 g. of the amide, 1.1 g. of acid (m.p. 144–149°) was obtained. After sublimation and two recrystallizations from acetone, the acid melted at 153–153.5° alone and when mixed with the acid obtained in part (a).

1,2,3,4-Tetrahydrophenanthrene-9-aldehyde. After an intimate mixture of 5 g. of the 9-acid anilide, 3.5 g. of finely powdered phosphorus pentachloride, and 4 cc. of dry benzene had been stirred until most of the mass had reacted to give a bright yellow oil, it was heated on a steam-bath for fifteen minutes. The benzene and phosphorus oxychloride were removed at 12–15 mm. by gradually heating the mixture to 140° and maintaining this temperature for 10–15 minutes. A cooled solution of the product in 8 cc. of ethylene dichloride was added to an ice-cold solution of 13 g. of anhydrous stannous chloride in 50 cc. of dry ether saturated with dry hydrogen chloride. The mixture was placed in a refrigerator; after an hour an orange crystalline solid started to separate. After forty-eight hours the complex (7.5 g.) was filtered from the solution and was hydrolyzed by hot dilute hydrochloric acid; yield 3.2 g. of tan powder; m.p. 125–129°. One recrystallization of the aldehyde from carbon tetrachloride-petroleum ether after treatment with Norit in the carbon tetrachloride gave 2.9 g. of long thin needles; m.p. 127–129°. After two recrystallizations from acetone-ethanol a sample melted at 128.5–129°. In addition 0.2 g. of anilide was recovered from the ethereal residue from the reaction.

Anal. Calc'd for $C_{15}H_{14}O$: C, 85.7; H, 6.7.

Found: C, 85.9; H, 6.7.

1,2,3,4-Tetrahydrophenanthrene-9- β -acrylic acid. A mixture of 2.5 g. of the 9-aldehyde, 2 g. of malonic acid, and 3 cc. of pyridine was heated on a steam-bath for eight hours. After a few hours, crystals of the product began to separate from the clear solution. The product was dissolved in 20 cc. of 5% sodium carbonate, the diluted solution was treated with Norit and the filtered solution was acidified; yield 2.75 g. (91%); m.p. 225–227°. After two recrystallizations from acetone a sample formed short colorless needles; m.p. 226.5–227.5°.

Anal. Calc'd for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4.

Found: C, 80.7; H, 6.4.

1,2,3,4-Tetrahydrophenanthrene-9- β -propionic acid. (a) *From the acrylic acid.* A solution of 0.5 g. of the acrylic acid in 10 cc. of 10% potassium hydroxide was shaken vigorously with 15 g. of 2% sodium amalgam for several hours; the filtered solution was then acidified. One crystallization from benzene-petroleum ether gave 0.46 g. of the reduced acid; m.p. 158–162°. After two more recrystallizations from acetic acid the acid was obtained in fine colorless needles; m.p. 168–169°.

Anal. Calc'd for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1.

Found: C, 80.4; H, 6.9.

The *methyl ester* prepared with diazomethane crystallized from methanol in long slender colorless needles; m.p. 49–50°.

Anal. Calc'd for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5.

Found: C, 80.4; H, 7.4.

(b) *From 9-chloromethyltetrahydrophenanthrene.* To a solution of sodium ethoxide prepared from 0.3 g. of sodium and 1.5 cc. of absolute alcohol and 1.3 cc. of benzene was added 3 g. of malonic ester and then 2 g. of 9-chloromethyl-1,2,3,4-tetrahydrophenanthrene in 3 cc. of benzene. After standing at room temperature for twelve hours the mixture was refluxed for twenty-four hours; 8.2 g. of potassium hydroxide, 5 cc. of alcohol, and 10 cc. of water were added and heating was continued for two hours. The benzene was evaporated and the residual solution heated another hour, diluted, filtered, and acidified. The dry dicarboxylic acid was decarboxylated at 180–190° for half an hour, the product was dissolved in benzene, the solution was extracted with 5% potassium hydroxide and the alkaline solution was acidified, whereupon the propionic acid precipitated; yield 1.7 g.; m.p. 158–162°. Two recrystallizations from acetic acid gave fine needles; m.p. 168–169°, alone and when mixed with the acid obtained in part (a). The methyl ester was obtained in needles; m.p. 49–50°, alone and when mixed with the ester obtained in part (a).

9-Acetyl-1,2,3,4-tetrahydrophenanthrene oxime. A mixture of 17.7 g. of 9-acetyl-1,2,3,4-tetrahydrophenanthrene, 14 g. of hydroxylamine hydrochloride, 70 cc. of absolute alcohol, and 23 cc. of pyridine was refluxed four hours on a steam-bath, most of the alcohol was distilled, and the residue was stirred with cold water until the oxime solidified. The oxime was crystallized from alcohol; yield 14.3 g.; m.p. 152–156°. Two recrystallizations from ethanol gave colorless prisms; m.p. 157–158°.

Anal. Calc'd for $C_{16}H_{17}NO$: N, 5.9. Found: N, 5.8.

9-Acetylamino-1,2,3,4-tetrahydrophenanthrene. After refluxing a mixture of 15.5 g. of the aforementioned oxime and 15.5 g. of phosphorus pentachloride in 300 cc. of dry benzene for fifteen minutes, the mixture was poured into cold water and stirred vigorously for several hours while the product precipitated. After standing for twelve hours, 9.2 g. of the acetylamino was filtered from the mixture, the benzene and aqueous layers were separated, and the benzene solution was washed with water, dried, and evaporated. On trituration with ether the residue yielded 2.3 g. of crude acetylamino, which was recrystallized to give an additional 1.5 g. of the pure compound; total yield 10.7 g.; m.p. 186–188°. Hydrolysis of the residue by refluxing it with 100 cc. of alcohol and 5 cc. of hydrochloric acid for twenty-four hours gave 1.2 g. of amine. The over-all yield of products amounted to 79%. A sample of the acetylamino recrystallized twice from ethanol formed fine colorless needles; m.p. 191–192°.

Anal. Calc'd for $C_{16}H_{17}NO$: N, 5.9. Found: N, 5.9.

9-Amino-1,2,3,4-tetrahydrophenanthrene. A solution of 13 g. of the 9-acetylamino derivative in 500 cc. of alcohol and 30 cc. of hydrochloric acid was refluxed for twenty-four hours. The alcohol was distilled and the residual amine hydrochloride was dissolved in a liter of boiling water and the solution was decolorized with Norit and filtered. The filtrate was cooled rapidly with crushed ice and the amine was precipitated with ammonium hydroxide. When the hot acid solution was allowed to stand in contact with the air and cooled slowly, fine needles of the amine hydrochloride separated, and both the solution and crystals became discolored. Yield of amine, 9.0 g.; m.p. 73–75°. After two recrystallizations from ethanol-methanol it formed clusters of colorless needles; m.p. 76.5–77°.

Anal. Calc'd for $C_{14}H_{15}N$: N, 7.1. Found: N, 7.2.

The *amine hydrochloride* after sublimation and two recrystallizations from alcohol formed stout colorless needles; m.p. 263–264°.

Anal. Calc'd for $C_{14}H_{16}ClN$: Cl, 15.2. Found: Cl, 15.3.

7-Acetylamino-1,2,3,4-tetrahydrophenanthrene. By treating a mixture (10.5 g.) of the 7- and 9-acetyltetrahydrophenanthrenes in the same manner as the 9-acetyltetrahydrophenanthrene, except that the oximes were not crystallized from alcohol, a mixture of acetylaminos was obtained from which the 9-acetylamino-1,2,3,4-tetrahydrophenanthrene was separated by crystallization from the benzene-water mixture (4.4 g.; m.p. 184–188°). The residue, after evaporation of the benzene, was recrystallized from methanol and gave 2.8 g. of impure acetylamino; m.p. 130–140°. Two recrystallizations from methanol gave 2 g. of colorless needles of the 7-acetylamino-1,2,3,4-tetrahydrophenanthrene; m.p. 136–137°.

Anal. Calc'd for $C_{16}H_{17}NO$: N, 5.9. Found: N, 5.8.

7-Amino-1,2,3,4-tetrahydrophenanthrene hydrochloride. The 7-amine was obtained as an oil upon hydrolysis of the 7-acetylamino in the same manner as for the corresponding 9 derivative. The amine hydrochloride was precipitated by passing hydrogen chloride into a benzene solution of the amine; after sublimation it was obtained in colorless needles by two recrystallizations from ethanol; m.p. 238–239°.

Anal. Calc'd for $C_{14}H_{16}ClN$: Cl, 15.2. Found: Cl, 15.1.

1,2,3,4-Tetrahydrophenanthrene-7-carboxylic acid. Using the hypochlorite method employed by Newman and Holmes (11), 7.5 g. of a mixture of the 7- and 9-acetyl derivatives was oxidized to the carboxylic acids; yield 6.5 g. of crude acids; m.p. 155–175°. By fractional crystallization from benzene-petroleum ether, one gram each of acids melting at 211–214° and 179–182° were obtained. Recrystallization of the former from acetone gave pure 9-acid (identical with the compound prepared from 9-cyanotetrahydrophenanthrene

above) melting at 214–215°; recrystallization of the latter gave colorless needles of the 7-acid, melting at 184–186°.

Anal. Calc'd for $C_{14}H_{16}O_2$: C, 79.6; H, 6.2.

Found: C, 79.3; H, 6.2.

The *methyl ester* obtained by the action of diazomethane crystallized from methanol in colorless prisms; m.p. 114–115°.

Anal. Calc'd for $C_{16}H_{18}O_2$: C, 80.0; H, 6.7.

Found: C, 79.9; H, 6.7.

1,2,3,4-Tetrahydrophenanthrene-7-acetic acid amide. This compound was obtained in the same manner as the corresponding 9 isomer from 7-acetyltetrahydrophenanthrene by the Willgerodt reaction. Two grams of the 7-acetyl derivative gave 1.4 g. (66%) of the 7-acetic acid amide; m.p. 205–210°. After sublimation under reduced pressure and two recrystallizations from acetone the amide was obtained in colorless needles; m.p. 210–211°.

Anal. Calc'd for $C_{16}H_{17}NO$: N, 5.9. Found: N, 5.9.

1,2,3,4-Tetrahydrophenanthrene-7-acetic acid. The acid was obtained by hydrolysis of the amide using acetic acid and hydrochloric acid as for the 9 isomer. Two recrystallizations from acetone gave fine colorless needles; m.p. 150–151°.

Anal. Calc'd for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7.

Found: C, 79.6; H, 6.8.

4-Keto-7,8,9,10-tetrahydroacephenanthrene (III). To 0.5 g. of the 9-acetic acid and one drop of pyridine in 3 cc. of dry ether was added 0.5 cc. of thionyl chloride, and the solution was allowed to stand for half an hour at room temperature. The excess thionyl chloride was removed under reduced pressure at room temperature and the crystalline acid chloride was dissolved in 15 cc. of anhydrous benzene. To this solution was then added 0.7 g. of anhydrous aluminum chloride in small portions with stirring and cooling in ice. After half an hour the mixture was kept at room temperature for thirty minutes and then hydrolyzed with ice and dilute hydrochloric acid. The product was evaporatively distilled at 160° and 0.05 mm. and crystallized from acetone-petroleum ether; yield 0.3 g. (67%); m.p. 157–159°. After two recrystallizations from acetone a sample was obtained in colorless fine needles; m.p. 158.5–160°.

Anal. Calc'd for $C_{18}H_{14}O$: C, 86.4; H, 6.4.

Found: C, 86.5; H, 6.3.

7,8,9,10-Tetrahydroacephenanthrene (IV). To 3 g. of amalgamated zinc, 5 cc. of acetic acid, and 5 cc. of hydrochloric acid was added a solution of 0.5 g. of the aforementioned ketone, in 3 cc. of toluene; the mixture was refluxed for twenty-four hours with the addition of 3 cc. of hydrochloric acid. The toluene layer was separated, the aqueous layer was washed with benzene, and the combined solutions were washed with water. After evaporative distillation under reduced pressure, the hydrocarbon crystallized from ethanol in colorless plates; yield 0.30 g. (63%); m.p. 88–89°. After two more recrystallizations it melted at 89–90°. The picrate formed red needles which melted at 111–112°. Fieser and Peters (4) reported 92.5° for the melting point of the hydrocarbon and 112° for its picrate.

SUMMARY

The reactions of several reagents with 1,2,3,4-tetrahydrophenanthrene have been studied and various new derivatives of the hydrocarbon have been prepared.

7,8,9,10-Tetrahydroacephenanthrene has been synthesized from 1,2,3,4-tetrahydrophenanthrene.

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REFERENCES

- (1) BACHMANN AND STRUVE, *J. Org. Chem.*, **4**, 472 (1939).
- (2) BACHMANN AND STRUVE, *J. Org. Chem.*, **5**, 416 (1940).

- (3) GRUMMITT AND BUCK, *J. Am. Chem. Soc.*, **65**, 295 (1943).
- (4) FIESER AND PETERS, *J. Am. Chem. Soc.*, **54**, 4373 (1932).
- (5) ZELINSKY AND TUROWA-POLLAK, *Ber.*, **58**, 1295 (1925).
- (6) MOSETTIG AND VAN DE KAMP, *J. Am. Chem. Soc.*, **55**, 3447 (1933).
- (7) HAWORTH AND MAVIN, *J. Chem. Soc.*, 1015 (1933).
- (8) BRADSHER AND AMORE, *J. Am. Chem. Soc.*, **63**, 493 (1941).
- (9) BACHMAN AND HOAGLIN, *J. Am. Chem. Soc.*, **63**, 621 (1941).
- (10) FIESER AND KILMER, *J. Am. Chem. Soc.*, **62**, 1354 (1940).
- (11) NEWMAN AND HOLMES, *Org. Syntheses*, **17**, 65 (1937).

